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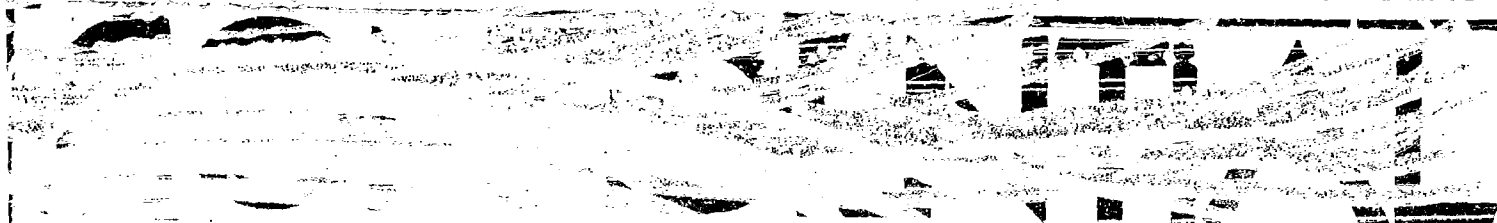
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TECHNICAL REPORT 2122

PILOT PLANT PREPARATION OF
POTASSIUM DINITROBENZOFUROXAN

MAURICE BAER

JANUARY 1955



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ORDNANCE PROJECT TA3-5001
DEPT. OF THE ARMY PROJECT 504-10-001

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PILOT PLANT PREPARATION OF
POTASSIUM DINITROBENZOFUROXAN

by

Maurice Baer

January 1955

Picatinny Arsenal

Dover, N. J.

Technical Report 2122

Ordnance Project TA3-5001

Dept of the Army Project 504-10-001

Approved:

for *to Carney*
for *for* *for*
JOHN D. ARMITAGE

Col, Ord Corps

Director,

Samuel Feltman

Ammunition Laboratories

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OBJECT

To prepare approximately 2 pounds of potassium dinitrobenzofuroxan (KDNEF).

ABSTRACT

Approximately two pounds of KDNEF was prepared. Benzofuroxan, made by the reaction of o-nitroaniline and alkaline sodium hypochlorite, was nitrated in a mixed acid. The product was recrystallized, and the potassium salt was made by reaction of this material with potassium bicarbonate. A yield of approximately 20% of theoretical was obtained. The loss was due to: (1) the solubility of benzofuroxan in the alcohol-water-sodium hydroxide solution and (2) the solubility of dinitrobenzofuroxan in cold (10°C) 70% nitric acid. Comparison of this product with the laboratory-prepared material indicated that the plant-prepared KDNEF was acceptable after filtration from the carbon tetrachloride desensitizer and washing with alcohol and ether.

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INTRODUCTION:

1. The use of various compounds as initiating explosives has been investigated at Picatinny Arsenal. One of the explosives studied was the potassium salt of dinitrobenzofuroxan (Ref A). Only small (50 gram maximum) quantities of the KDNBF could be prepared in the laboratory, although larger amounts of uniform quality were required for tests. It was decided that approximately two pounds should be prepared in pilot-plant equipment by the process that had been used to prepare suitable material in the laboratory. As only one batch was to be made, this precluded any possibility of a process study. This report covers the observations made in the various steps of the process, and the results of analysis of the final product.

DISCUSSION:

2. The first batch of benzofuroxan was prepared with factory alcohol and o-nitroaniline, both as received. The o-nitroaniline for this batch was not screened before being added to the saturated solution of sodium hydroxide in alcohol and did not completely dissolve even after 2.5 hours of agitation. A red, gelatinous precipitate due to iron present in the alcohol obscured the course of the reaction when the sodium hypochlorite was added. For this reason, the end point of the reaction, the precipitation of yellow crystals and the disappearance of the red-colored solution, could not be observed. After dilution, filtering, and washing, the resulting benzofuroxan appeared normal. The material was placed on trays in a forced-circulating air dry house at 60° to 65°C. The next morning only a small amount of material remained on the trays and this contained relatively large amounts of iron oxide. The material had evidently sublimed. Observation under a microscope of the melting of the compound showed that the crystals melted at 68°C, and, at a slightly higher temperature, rapid vaporization of the resulting liquid occurred.

3. Another run was made with clean 200-proof alcohol and 4.5 pounds of o-nitroaniline which had been screened through a No. 45 sieve. Complete solution was readily obtained and no lumps were formed. When the hypochlorite (laundry bleach) was added, yellow crystals formed and no trace of red coloration remained.

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The product was air-dried in thin layers at ambient temperature. Two and one-half pounds of benzofuroxan, 56% of the theoretical yield, was prepared. It was noted, however, that when the mother-liquor (water-alcohol-sodium hydroxide) was further diluted with water, more material was precipitated.

4. No difficulty was encountered during nitration of the benzofuroxan. The nitration slurry was drowned in water containing crushed ice. As this is not considered good plant practice, it is recommended that the use of service water at ambient temperature, summer or winter, should be investigated. Recovery of the dinitrobenzofuroxan without drowning should also be studied in order that the spent acid may be fortified and economically re-used.

5. Five pounds of water-wet, crude dinitrobenzofuroxan (DNBF) containing 10 to 20% water was obtained for a yield of approximately 96%. When the crude DNBF was recrystallized from 70% nitric acid, more than half the material was lost; only 1.3 pounds of wet material was recovered. The material precipitated from the nitric acid by drowning in water was not used, as the melting point was 108° to 113°C versus 170°C for the recrystallized product (172°C is the reported value for DNBF). The nitrogen content of the precipitated material was 19.42%, whereas that of the recrystallized product was 23.50% (24.8% nitrogen, theoretical). Another reason for the low yield was that a small kettle was not available for the recrystallization and a large excess of 70% nitric acid was necessary to obtain proper agitation.

6. Conversion of the DNBF to the potassium salt offered no difficulty. Approximately 1.5 pounds was obtained, which is 100% of theoretical yield. The overall yield for the entire process was 20% of theoretical.

7. The final product was desensitized by being stored under carbon tetrachloride. It was noticed that the supernatant liquid was dark, whereas the material produced in the laboratory did not color the carbon tetrachloride. When a sample of the material was withdrawn and the desensitizer removed by evaporation, analysis showed the material to be impure. When the carbon tetrachloride was removed by filtration, however, the product was comparable to the material prepared in the laboratory, as indicated by data given in Table 1.

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8. It is believed that the over-all yield can be materially raised by changes in the process resulting from a study of the following factors:

a. Use of a larger volume of water to precipitate the benzofuroxan from the sodium hydroxide-alcohol solution. The effect on the purity of the benzofuroxan should be determined.

b. Use of other conditions for the nitration of benzofuroxan. The poor quality of the DNEF precipitated from the 70% nitric acid may have been caused by under-nitration as well as by the formation of by-products.

c. Use of other solvents to recrystallize the DNEF, as its solubility in nitric acid is quite high, even at very low temperature. The need to recrystallize DNEF may be eliminated by a study of the nitration to substantially reduce the amount of impurities present.

d. Use of equipment to fit the process instead of improvised process equipment.

9. The procedure given in the following paragraphs is an adaptation of the one used in the laboratory. Variations stated in the preceding paragraphs were made as a matter of expediency, i.e., equipment size, loss of material due to sublimation of the benzofuroxan, and low yields. It was originally intended to prepare 10 pounds of the dinitro acid compound, as its explosive properties approximate those of tetryl, and to prepare smaller amounts of the potassium salt.

10. A 200X photomicrograph of the KDNEF produced, Figure 1, shows the crystal shape of this material.

EXPERIMENTAL PROCEDURE:

11. MATERIALS:

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O-nitroaniline--c.p.

Sodium hypochlorite, 5 to 11%--commercially available as laundry bleach

Alcohol - Purchase Description PA-PD-165 with Amendment 1 dated 3 February 1953

Sulfuric acid, 96%, Grade 1 -Specification JAN-A-179 dated 31 January 1945

Nitric acid, Class b - Specification JAN-A-183 dated 28 February 1945

Nitric acid, 70% - c.p.

Potassium bicarbonate - c.p.

Sodium hydroxide pellets - c.p.

12. EQUIPMENT:

Nitrator - The nitrator was a 55-gallon, jacketed, stainless steel vessel equipped with an air-driven, propeller-type agitator. (Note: All the reactions were carried out in this vessel).

Drowning Tub - This piece of equipment was a 200-gallon stainless steel tank equipped with an agitator.

Vacuum Filter - The filter was an open, 30-inch-diameter, stainless steel vacuum pan filter with a close-weave cotton twill cloth.

13. PROCEDURE:

Preparation of Benzofuroxan - Seventy-nine pounds of alcohol was added to the nitrator, the agitator started, and the speed adjusted to 50-60 rpm. Fifteen pounds of sodium hydroxide

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was added slowly, and when solution was obtained, eight-ounce increments of sodium hydroxide were added until the alcohol was saturated. Each increment was allowed to dissolve before the next was added. Brine was passed through the jacket to prevent the temperature from exceeding 50°C, and when saturation was obtained, the temperature was lowered to 10°-20°C, where it was kept throughout the reaction. Ten pounds of o-nitroaniline was added and agitation continued until complete solution was obtained. Sodium hypochlorite was then added, with agitation, until the color of the solution was yellow and no trace of red remained. The solution was then diluted with 100 pounds of cold (10° to 20°C) water and filtered. The material was washed with 1-gallon portions of cold water until neutral to litmus, each wash being removed before the next was added. The material was aspirated on the vacuum pan for 1 hour and then spread in thin layers to dry at ambient temperature.

Nitration of Benzofuroxan - One hundred ten pounds of 96% sulfuric acid was added to the nitrator, the agitator started, and the temperature lowered to 0°-5°C by passing brine through the jacket. Ten pounds of the dry benzofuroxan was added and agitation continued until complete solution was obtained, with the temperature maintained between 0° and 5°C. Ninety-seven pounds of mixed acid (prepared by mixing 23 pounds of 98% nitric acid and 74 pounds of 96% sulfuric acid) was slowly added to the nitrator at such a rate as to maintain the temperature between 0° and 5°C with brine flowing through the jacket. When all the acid had been added, the temperature was raised to 40°C by passing steam through the jacket. This temperature was maintained for one minute, and then the reaction mixture was drowned in 75 gallons of agitated cold water containing 75 to 100 pounds of crushed ice. The precipitated material was filtered and washed on the vacuum pan with one-gallon portions of cold (10°C) water until neutral to litmus. Each wash was removed by vacuum before the next was added. The neutralized material was aspirated for 2 hours to remove the excess water. The filtrate and washings were neutralized to a pH of 6.5, transferred to a sawdust-filled can, and sent to the burning grounds.

Recrystallization of DNEF - Fifty pounds of 70% nitric acid was transferred to the kettle, the agitator started, and the crude dinitrobenzofuroxan slowly added. The mixture was heated to 68°-70°C by passing steam through the jacket. Agitation was

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continued until solution was complete. The solution was cooled to 10°-15°C by passing brine through the jacket of the kettle. It was then filtered and the filter cake washed as above.

Preparation of KDNEF - Fifty pounds of water and one pound (dry weight) of the recrystallized DNEF were added to the jacketed vessel. The mixture was heated to 70°-75°C by passing steam through the jacket. Then 8 ounces of potassium bicarbonate was added and the mixture was agitated until there was no further evolution of carbon dioxide. The mixture was then cooled to 5° - 10°C by passing brine through the jacket of the kettle. Filtering and washing were accomplished as above, except that a 12-inch Buchner funnel equipped with a close-weave cotton twill cloth was used. After aspirating the material for 10 minutes on the funnel, 1 quart of alcohol was added; then vacuum was applied until all the alcohol was removed. One quart of ether was then added, vacuum again applied, and the material aspirated until dry. The material was then wet with 1 quart of carbon tetrachloride and transferred to wide-mouth glass containers which were closed with cork stoppers.

REFERENCES:

A. Gaughran, R. J., Abel, J. E., and Forsyth, A.C., Development of Optimum Explosive Trains, Picatinny Arsenal Memorandum Report MR-43, 30 September 1953.

INCLOSURES:

1. Table 1
2. Figure 1

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TABLE 1

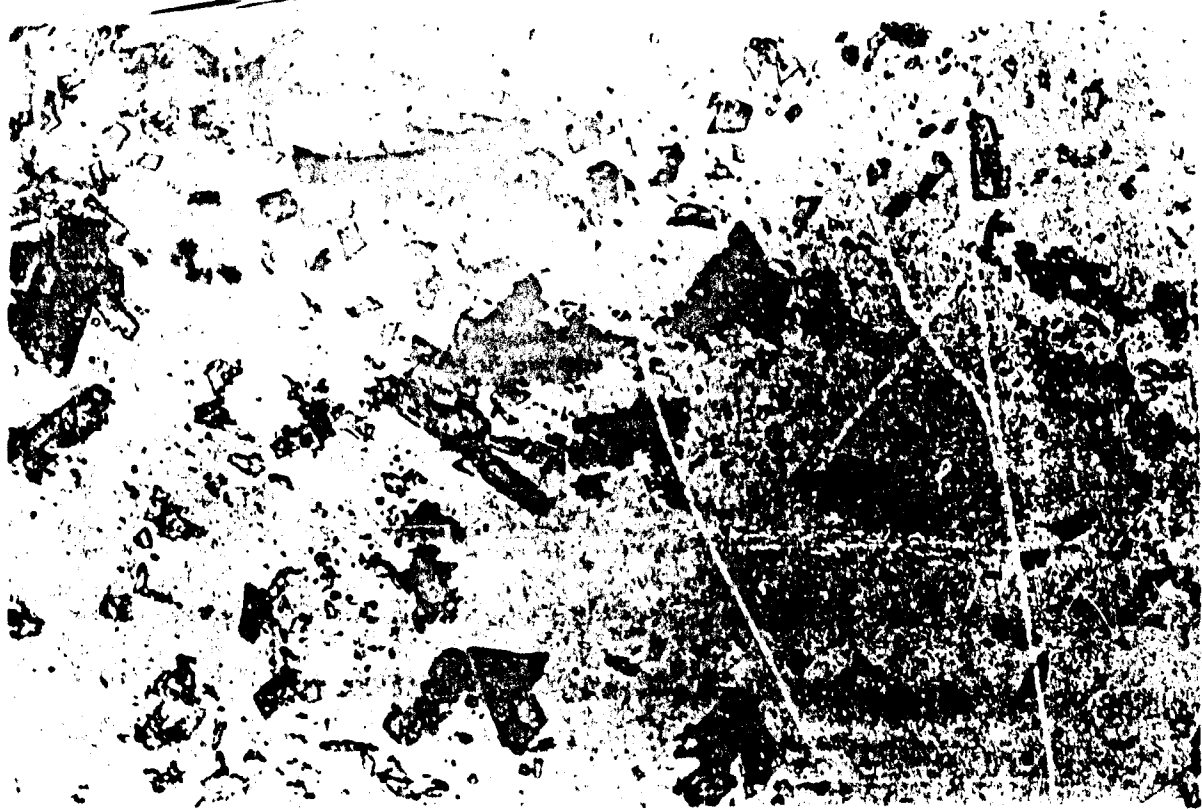
Characteristics of Potassium Dinitrobenzofuroxan (KDNBF)

	<u>Prepared in Plant</u>	<u>Prepared in Laboratory</u> ^a
Explosion Temperature, °C	245	250
Impact Sensitivity:		
P. A. Apparatus, 2 kg wt, in	3	3
Charge weight, gm	0.009	0.007
P. A. Apparatus, 1 lb. wt, in	8	6
Charge weight, gm	0.009	0.006
Brisance by Sand Test:		
Sand crushed, gm	44.4	44.8
Initiating charge, lead azide, gm	0.300	0.300
Hygroscopicity:		
At 90% RH, 30°C	0.00	0.27
At 70% RH, 30°C	0.00	0.11
100°C Heat Test:		
1st 48 hours, % loss	0.40	0.30
2nd 48 hours, % loss	0.23	0.05
Explosion, 100 hrs	none	none
Solubility in Water		
gm/100 gm water at 30°C	0.25	0.25
Potassium, %	15.22 ^b	14.83
Heat of Explosion, cal/gm	671	725
Heat of Combustion, cal/gm	2361	2209

a Data obtained from Reference A.

b Theoretical 14.90% potassium

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M-45699 Oct. 1954

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Photomicrograph of Potassium Dinitrobenzofuroxan

Fig. 1

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Magnification: 200X

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